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A REVIEW OF MIXED MATRIX MEMBRANES IN GAS SEPARATION

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ABSTRACT

The aim of this research is for the separation of oxygen from sulfur dioxide (SO₂) and carbon dioxide (CO₂) is preparing a novel mix matrix membrane (MMC) using novel microwave technique. Mix membrane polymer can develop, by using PVDF (Polyvinylidene Fluoride) and Polycarbonate (PC). The performance of the mix membrane polymer will evaluated in terms of the separation rate of oxygen. In order to investigate the influence of microwave technique on the mechanism of mix membrane polymer; FTIR, NMR will performed. In addition the membrane morphology and structure will examined using SEM, FTIR and NMR. The gas separation properties will be measure using lab scale test rig.

Keywords: Gas separation, mixed matrix membranes, permeation rate, selectivity

INTRODUCTION

Nowadays the cost of energy consumption increasing rapidly, membrane technology for separating gases is likely to play an increasingly important role in reducing the environment impact and costs of industrial processes. Compare to other membrane technologies like reverse osmosis and ultrafiltration, commercial gas separation using membrane is relatively new (Lonsdale, 1982). Gas separation membranes provide numerous of benefits over other gas separation technologies. This membrane technology has been applied commercially to separate individual components from mixtures of gases. The membranes are non-porous thin layers on porous substrates. Three major elements required for a commercial gas separating membrane, there are high permeability, high selectivity and good mechanical strength (Kesting et al., 1993). The development of asymmetric membranes greatly improves the permeation rate without sacrificing the selectivity (Pesek, 1993).

One the years, a great variety of different types and classes of membrane have been developed and reported. Membrane can be classified in various ways (Matson et al., 1983). For gas separation, membranes can be solid (polymetric or inorganic or metallic) or liquid. Solid membranes can be non-porous, microporous, asymmetric, or composite. Liquid membranes can have different structure, e.g., immobilized or supported liquid membranes, emulsion liquid membranes and contained liquid membranes (Noble et al., 1995). Separation of mixtures of gases is potential using either porous or non-porous membranes although there have different mechanism of transport that involved. Separation in porous membranes is through the difference in Knudsen flows (diffusion) of the components in the pores which are of a size less than the mean free paths of the molecules. The flux of individual gases is inversely proportional to the square root of the relative molar mass for a

given membrane, temperature and pressure driving force. Hence generally low separation factor are obtained with most gas mixture except those containing hydrogen and helium. Non-porous membranes are used in many commercial applications for the separation of gas mixtures. Separation of gases through non-porous membranes depends on the different in permeability of the constituent gases. Gas permeation (GP) is the only means by which membranes can be used to separate gas mixtures without a change in phase. Separation of different gases is achieved by virtue of differences in molecular size and gas solubility in the membrane. The smaller molecular sizes of gases have larger diffusion coefficients and in convection free environment in the pores of a membrane can be suitably separated by virtue of the different mobility (Scott, 1998).

MEMBRANE FABRICATION

Hollow Fiber Membrane Fabrication

The spinning of Hollow fibers is very frequently applied as a preparation technique for UF membranes. Even so the number of essential contribution to this matter is incomplete (Wienk et al., 1995 and Wood et al., 1993). Much knowledge about the spinning of porous hollow fiber membranes has been described in patents. In the spinning process both phase separation and rheological phenomena will have an influence on the shape and morphology of the membrane fibers (Xu and Qusay, 2004). There are different parameters in the process of hollow fiber spinning that can affect separation performance. Most hollow fiber membranes are prepared by the so-called dry-wet spinning process and only few have been prepared by a wet-wet or dual bath spinning process (Li et al., 1994 and van't Hof et al., 1992)

The hollow fiber configuration is the favorite choice for modules in membrane separation because of the hollow fiber membranes having three major advantages over flat sheet membranes (Chung et al., 2000);

- (i) hollow fibers have much larger ratio of membrane area to unit volume and hence higher productivity per unit volume of membrane module;
- (ii) there is self supporting that can be back-flushed for liquid separation;
- (iii) they have good flexibility in operation. Therefore, the key properties determining membrane performance are high selectivity and fluxes, good mechanical strength, good chemical resistance, thermal stability under operating conditions, low fouling tendency, good compatibility with the operation environment, cost effective and defect free production (Strathmann, 2001).

PREVIOUS STUDY OF MODIFICATION MIXED MATRIX MEMBRANE

There numerous of researches that has been done since year 2002 in gas separation using mixed matrix membranes. Mixed matrix membrane is a biggest step of improvement gas separation technology compare using single membrane in gas separation system. From year to year experimental have been done in order to get the best permeability and selectivity during of gas separation. The modification also focuses on economical cost that lower cost much better and beneficial. This paper will discuss and explain previous study achievement by highlight their successful modification.

Achievement of year 2002

Modification of Glass Transition Temperature (T_g)

De Q. Vu (De Q. Vu et al., 2002) produced mixed matrix membrane (MMM) films for gas separation by integrated Carbon molecular sieves (CMSs) into two different polymer matrices (Matrimid 5218 and Ultem 1000). The CMSs were produced by pyrolysis of a polyimide (Matrimid) to a final temperature of 800°C. These membrane films have an intrinsic CO₂/CH₄ selectivity of 200 with a CO₂ permeability of 44 Barrers and an O₂/N₂ selectivity of 13.3 with an O₂ permeability of 24 Barrers at 35°C. These two mixed matrix membrane were tests by pure gas permeation and the results show enhancements by as much as 40% in CO₂/CH₄ selectivity using Ultem-CMS MMM over the intrinsic CO₂/CH₄ selectivity of the pure Ultem polymer matrix. Enhancements 45% in CO₂/CH₄ were observed by Matrimid- CMS mixed matrix films. These mixed matrix membrane films also were examined for the O₂/N₂ separation and showed enhancements 8 and 20% for Ultem – CMS and Matrimid – CMS mixed matrix membrane respectively. The CMSs were prepared by pyrolysis CMS membrane to 800°C for 2h. CMS 800-2, lies well beyond Robeson Upper bound with 200 selectivity of CO₂/CH₄ and 43.5 Barrer of CO₂. The T_g of the matrix polymers increased with the incorporation of the CMS particles. This T_g elevation phenomenon is observed in semi-crystalline polymers with the proportional increase in crystallinity. The present of a dispersed constituent (e.g. CMS particle) can affect the fundamental properties (e.g. T_g) of the continuous polymer matrix phase when good segmental-level attachment exists between these two phases. Ultem-CMS increase T_g about 2-5°C above that of pure Ultem with increment of CMS loading and Matrimid-CMS increase significantly T_g about 15°C and as the result increase the permeability and the selectivity of these pure membranes.

Achievement of year 2002

Modification of synthesis method and the membrane casting conditions

Hacarlioglu et al. (2003) conducted a gas separation experiment by using polycarbonate-polypyrrole mixed matrix membranes. The gas separation properties were evaluated based on the induction of conducting polymer as power filler. There two routes were used in order to obtain the electrically conductive fillers are namely electrochemical and chemical method. The synthesis method (electrochemical or chemical) and the membrane casting conditions (casting solvent type) were highly influence the permeation properties of the polycarbonate-polypyrrole system. Higher permeation rate of electrochemically synthesized polypyrrole-polycarbonate (ECPY-PC) were achieved compared to both pure polycarbonate (PC) and the chemically synthesized polypyrrole-polycarbonate (CPY-PC) films accompanied with a loss in selectivity by distorted the polycarbonate matrix via forming cavities. Besides that, an improvement of the selectivity of industrially important gas pair (H₂/N₂, O₂/N₂ and H₂/CH₄) result of the densified structure of CPY-PC. Polypyrrole films were electrochemically synthesized by galvanostatic technique which supplies and controls the electrolysis current. A two electrode, one compartment cell was employed with a horizontally oriented stainless steel type 304 anode. Stainless steel wire mesh gauze suspended above the anode was employed as the cathode. Ten milliliters of pyrrole and 0.05M p-toluenesulfonic acid were mixed in 800 ml of aqueous solution. During the preparation of the supporting electrolyte, the pH of the solution was adjusted to

11 by adding 0.05M NaOH to completely deprotonate PTSA into the anion form. The syntheses were carried out at a current density of $2.0\text{mA}/\text{cm}^2$ at room temperature for 2 h. The current was supplied from a regulated dc power supply. The freestanding polymer film formed by this way could easily be peeled off the anode, washed thoroughly by distilled water and dried. Further, these films crushed into powder form in liquid nitrogen.

Achievement of year 2005

Implementation of Heat Treatment and Coating

An experimental conducted by Lan et al. (2005) to enhanced selectivity for He/N_2 and O_2/N_2 separation have been developed by produced hollow fiber with a thin zeolite beta-polysulfone mixed matrix selective layer. The heat treatment and the coating processes combine to bring out the separation properties of zeolite beta imbedded in the polymer matrix. Initially, the fibers were formed by using the dual-layer co-extrusion and dry-jet wet/wet spinning technology. Through SEM analysis, showed that heat treatment at above T_g can significantly densify the loose mixed matrix layer and produced hollow fibers with a thin matrix selective layer of around $1.5\text{-}12\mu\text{m}$, but did not produce defect-free hollow fiber membranes. The sealing of the mixed matrix outer layer is confirmed to be the cause for the selectivity increment instead of the caulking of the inner layer. In other hand, it is also observed that the thickness of the mixed matrix composite outer layer influence permeability and selectivity. Besides that, the activation energies (E_p) for O_2 and N_2 calculated from the permeance or permeability at different temperatures indicate that the addition of zeolite beta in the polysulfone has reduced the energy barrier for O_2 permeation.

The as-spun fibers were taken by a drum and then cut into segments and rinsed in a clean water bath for at least 5 days to remove the remaining solvent. Solvent exchange was carried out by first using methanol three times, each time with 30 min, then n-hexane three times, each time 30 min. After being taken out from the hexane, the fibers were dried in the air at room temperature. The as-spun fibers have high permeance without much selectivity. Therefore, the resultant hollow fibers were annealed at 130 , 150 and 200°C for 12, 6 and 2 h, respectively, to diminish the surface defects. In addition, the three coating processes were employed and their effectiveness to seal the membrane defects was compared. The solution of the coating approaches A and B contains 2wt. % silicon rubber in hexane and iso-octane, respectively; while the solutions for the two-step approach C are (1) 0.2wt.% diethyltoluenediamine in iso-octane and (2) a mixture of 0.2wt.% of 1,3,5-benzenetricarbonyl chloride and 2wt.% silicon rubber in iso-octane. Each step of coating was conducted by dip coating the fiber when applying vacuum from the fiber lumen for 30min. This concept of reactive coating was first proposed by DuPont scientists and later applied on sealing the mixed matrix membranes. The fibers coated with the method A were kept in a dry box for 2 days before testing; the fibers under methods B and C were annealed at 100°C for 2 h before gas separation characterization. The heat treatment processes were all performed in a precision high-temperature programmable furnace (Centurion TM Neytech Qex) under vacuum.

Achievement of year 2005

Dual-layer Hollow Carbon Fiber Membranes with Additive (Single Membrane)

Membrane separation method is among the effective ways of fluid separation. Beyond of the molecular separation, world today exciting on finding more effective methods of separation which can be developed deeps into the atomic separation. Dual - layer hollow carbon fiber membranes is a gas separation method with an enhanced performance with minimum structure resistance. This method using (6FDA-ODA-NDA)/polysulfone (PSF) dual layer hollow fiber membranes as the investigated subject. Based on its balanced in chemical and mechanical properties as well as low cost, a high performance polyimide, (6FDA-ODA-NDA) copolyimide = 50/50 is used as the outer selective layer material while PSF is chosen as the inner layer material. Using Al₂O₃ nanoparticles in the inner dope solution as an additive can lower the structure resistance and few cases may achieve 90% of the intrinsic selectivity (Natalia Widjojo.et.al). In addition, they are inexpensive and readily available materials. Besides increase bulk and surface porosity, a better interface interaction and balanced stress distribution can achieve maximum take-up speed and will be increased two fold of the elongational draw ratio.

Achievement of year 2005

Dual-layer Hollow Carbon Fiber Membranes with Zeolite Beta (Mixed Matrix Membrane)

Using dual-layer hollow carbon fiber membranes as for gas separation have been successfully approved in its effectiveness. Composed of Polysulfone- zeolite beta (PSF-BETA) mixed matrix in the outer layer and a matrimid inner layer, gives much better performance compared to the hollow carbon fiber derived from single-layer matrimid hollow fiber. Simply description about the process, after the pyrolysis the PSF-beta layer in the dual-layer precursor evolces into continuous structure of closely packed zeolite particles embedded in the PSF carbon residue. This combination give higher in selectivity simultaneously increase the separation performance. The independent PSF-beta outer layer cannot form any continuos structure after pyrolysis under the same condition because polysulfobe decompose rapidly. Before pyrolysis process, matrimid result in fully porous and nonselective structure in the inner layer. It also exhibit Knudsen diffusion, but much lower permeance. That condition said that a higher PSF concentration resulting in higher gas transport resistance, while the beta zeolite – PSF interface defects cause low selectivity. Pyrolysis process will create high flux of precursors. This will give lower in gas permeability and enhance the selectivity. This circumstance explained that the thermal decomposition patterns and paths for both PSF-beta/matrimid at difference state will give difference structures. In addition, shrinking of the PSF-beta outer layer will results in the collapse of the microporous and the alignment of the microdomains, thus will create more small pores.

Table 1: Differences between both types are:

Characteristics	(6fda-oda-nda)/polysulfone (pfs)	Polysulfone-beta zeolite (psf-beta)/matrimid
Selectivity	High to 90%	Higher than single layer membranes
Costing	Lower in cost	Higher in cost
Availability	Excellent	Good
Process	Simple	Simple

CURRENT STUDY OF HOLLOW FIBER MIXED MATRIX MEMBRANE

The current study is fabrication of hollow fiber mixed membrane polymer by using PVDF (Polyvinylidene Fluoride) and Polycarbonate (PC). Polyvinylidene Fluoride (PVDF) is a highly non-reactive and pure thermoplastic fluoropolymer. The specialty of this PVDF is used generally in applications requiring the highest purity, strength, and resistance to solvents, acid, bases and heat and low smoke generation during a fire event. Compared to other fluoropolymer, it has easier melt process because of its relatively low melting point of around 177°C. Besides that, it has a low density (1.78) and low cost compared to the other fluoropolymers. It also can be injected, molded or welded and is commonly used in the chemical, semiconductor, medical, defense industries and lithium ion batteries industries. PVDF is a very attractive polymer, exhibiting chemical and mechanical resistances, widely used to synthesize membranes for various membrane operations. Nowadays the phase inversion technique is commonly used to prepare PVDF membranes.

Polycarbonates (PC) are a particular group of thermoplastic polymers. This polymer easily worked, moulded, thermoformed and widely used in the modern chemical industry. Their interesting features such as temperature resistance, impact resistance and optical properties place them between commodity plastics and engineering plastics. Their plastic identification code is 7. This polymer received their name because having functional groups linked together by carbonate groups (-O-(C=O)-O-) in a long molecular chain. Polycarbonates membrane always been used in separating the oxygen. We have previously reported that transition metal additives in a polycarbonate casting solution are capable of improving the oxygen permeability by dry-phase inversion. In addition; wet-phase inversion is used in preparing asymmetric membrane to improve the gas separation and evaporation performance. This mixed matrix membrane will be integrated with several of modification such as heat treatment, additive and dual-layer of hollow fiber mixed matrix membrane.

Membrane Testing

Figure 2 shows the test system used to evaluate the performance of the gas permeation rate. Source of CO₂ supply from CO₂ tank and the pump will increase the pressure of the gas before entering the hollow fiber module. The permeated gas will collect using sampling bag in order to analyzed using gas chromatography.

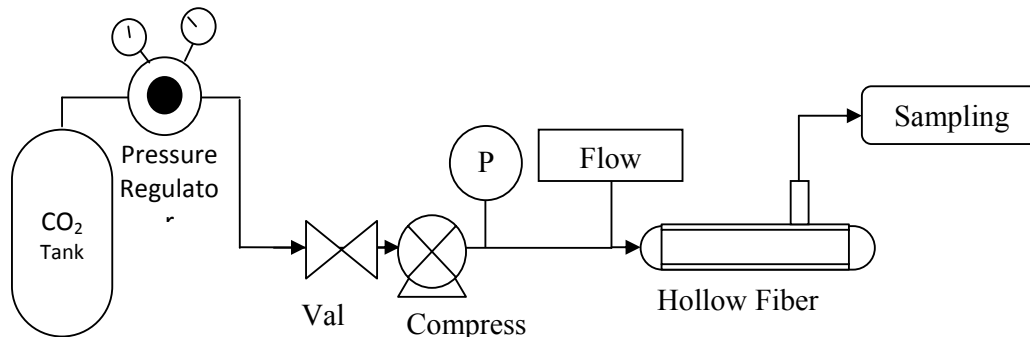


Figure 2: A schematic diagram of membrane testing

Methodology

The schematic diagram as depicted in Figure 3 is also summarizing the methodology of this project

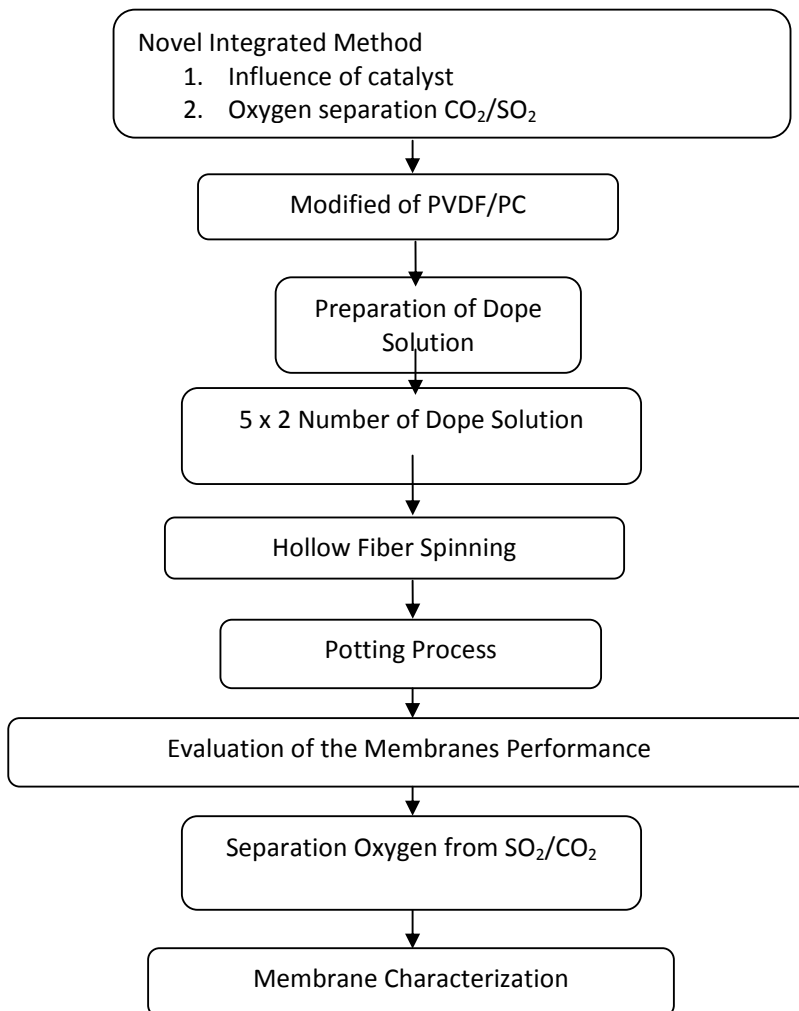


Figure 3: Schematic Diagram for the Research Methodology

Expected result

Mixed matrix membrane that has double layer of hollow fiber with integration of heat treatment, additive, modification of synthesis method, membrane double coating, membrane casting conditions and modification of glass transition temperature is expected that will increase the permeability and the selectivity of gas separation.

CONCLUSION

All modification brings good effect to the permeation rate and selectivity. There a lot of possibility can happen by modify the original members. In future, all the modification should be combined in order to get the better membrane for gas separation system. At the moment, the world of gas separation system will move further to the next level of gas separation.

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